DESCRIPTION

GLASS FOR MULTILAYER FILM FILTER AND METHOD FOR MANUFACTURING THE GLASS

TECHNICAL FIELD

The present invention relates to glass for a multilayer film filter and a method for manufacturing the glass.

BACKGROUND ART

A multilayer film filter transmits or blocks light having a specific wavelength, or changes light intensity regardless of wavelengths. Multilayer film filter chips are obtained by alternately forming low refractive index films such as SiO_2 and high refractive index films such as TiO_2 or Ta_2O_5 onto the top surface of a substrate by sputtering or evaporation, and then by dividing with a dicing cutter.

The conventional glass substrate for a multilayer film filter has a large thermal expansion coefficient. The reason for this is to reduce the amount of shift in filtering properties with temperature changes (hereinafter referred to as wavelength shift). An example of glass of this type is disclosed in Japanese

Patent Laid-Open Application No. 2001-48584.

Figs. 1 and 2 show changes in filter properties with temperature changes. In many filters, as shown in Fig. 1, filtering properties 21 make a large shift in the positive direction with a temperature increase so as to change into filtering properties 22. A large amount of shift means that the filter properties change greatly with temperature changes. Therefore, when the wavelength shift is large, the filter can be used as a filter having required properties only in a narrow temperature range. In other words, a filter making wavelength shift closer to 0 can be used as a filter having required properties in a wider temperature range.

It is known that the larger the thermal expansion coefficient of the glass for a multilayer film filter than the thermal expansion coefficient of the multilayer film is, the longer the wavelength shift which occurs in the negative direction becomes. On the other hand, the thermal expansion coefficient of the glass used as a substrate is generally around $100\times10^{-7}/°C$ in the temperature range of 50°C to 150°C, and the wavelength shift often has a positive value. When the wavelength shift occurs in the positive direction, a substrate having a thermal expansion coefficient not lower than $100\times10^{-7}/°C$ is required for having the shift value close

to 0.

In a case where more complicated properties are required as the filter properties, it is necessary to increase the number of layers in the multilayer film, thus leading to an increase in film thickness as a whole. In general, in forming a multilayer film onto the glass for a multilayer film filter, the amount of wavelength shift increases with increasing thickness of the multilayer film. From this reason, the thermal expansion coefficient of the glass for a multilayer film filter is preferably larger than that of the conventional glass material. Using such glass having the larger thermal expansion coefficient makes it possible to obtain a filter having a small shift as shown between filter properties 31 at a low temperature and filter properties 32 after a temperature rise in Fig. 2.

On the other hand, it is possible to maintain light transmittance and to improve the thermal expansion coefficient by crystallizing the glass partially to make small particles which have a large thermal expansion coefficient for a multilayer film filter. Such partially crystallized glass is sometimes used as the glass for a multilayer film filter. Even in that case, the highest thermal expansion coefficient of the partially crystallized glass is about $125\times10^{-7}/°C$ in a

temperature range of 50°C to 150°C so far, and there are cases where the wavelength shift of the multilayer film filter cannot be fully reduced.

SUMMARY OF THE INVENTION

Glass for a multilayer film filter according to the present invention is partially crystallized glass which is made from SiO_2, B_2O_3, Na_2O, K_2O, MgO and Al_2O_3 and has a mean linear expansion coefficient of not lower than $125\times10^{-7}K^{-1}$ in the temperature range of 50°C to 150°C. In this composition, potassium aluminum silicate base crystals are partially precipitated, so as to make the thermal expansion coefficient of the glass high. Such glass can be obtained by cooling and solidifying a glass melt so as to form glass; immediately cooling the obtained glass slowly; heating the glass up to a temperature higher than its glass transition temperature and keeping the temperature for a prescribed period of time; and slowly cooling the glass at a prescribed rate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 2 show changes in filter properties with temperature changes.

Fig. 3 is a cross sectional schematic view of a multilayer film filter chip using a glass as a substrate

according to an embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

As shown in Fig. 3, a multilayer film filter chip is obtained by alternately forming low refractive index films 12 and high refractive index films 13 onto the top surface of substrate 11 by sputtering or evaporation, and then by dividing with a dicing.

The glass used as substrate 11 is prepared as follows. First of all, SiO_2, B_2O_3, Na_2O, K_2O, MgO and Al_2O_3 as glass ingredients are mixed in various compositions that weigh 200g in total. The mixture of glass ingredients is melted for 30 minutes at 1550°C, poured into molds, quenched for vitrification and immediately annealed over 24 hours from a glass transition temperature to room temperature. This results in glass blocks from which the remaining strain has been removed.

Next, the glass blocks are subjected to a reheating treatment for crystallization. In that case, the glass blocks are put in a furnace for the reheating treatment, heated from the room temperature up to a retention temperature over the glass transition temperature at 100°C/h, kept at the temperature for a fixed period of time and annealed to the room temperature. This reheating treatment is applied to the glass compositions

under some different retention temperatures, retention times and slow cooling rates.

The following is a description of the compositions of the partially crystallized glass. In each glass, SiO_2 and B_2O_3 function as glass forming oxides. When the amounts of SiO_2 and B_2O_3 added are very small, the mixture of glass ingredients does not melt, or even if it melts, the melt crystallizes immediately when it is poured into the molds and does not vitrify. In contrast, when the amounts are very large, the glass does not crystallize in the reheating treatment process. When the amount of B_2O_3 is very small relative to the amount of SiO_2, the glass melting temperature increases, making it difficult to obtain uniform glass. In contrast, when the amount of B_2O_3 is very large relative to the amount of SiO_2, phase separation can occur while the mixture of glass ingredients is melted. Even when the mixture of glass ingredients successfully forms into glass, the glass does not crystallize in the subsequent reheating treatment process.

K_2O has the effect of increasing the thermal expansion coefficient of glass, and becomes a component of crystals to be formed at the reheating treatment. However, adding a very large amount of K_2O is unpreferable because it deteriorates the water durability of the glass.

Na_2O has the function of decreasing the glass melting temperature and increasing the thermal expansion coefficient; however, its effect of increasing the thermal expansion coefficient is not so large as that of K_2O. Therefore, when the amount of Na_2O added is very large relative to K_2O, the linear expansion coefficient of the glass is not large enough. Furthermore, adding a very large amount of Na_2O deteriorates the water durability of the glass. When the total amount of Na_2O and K_2O added is very small, it becomes difficult to melt the mixture of glass ingredients. In contrast, the total amount is very large, the glass melt is prone to crystallize at the time of being poured into the molds, and also decreases the water durability of the glass.

MgO has the effect of facilitating the partial crystallization of glass in the reheating treatment process. However, adding a very large amount of MgO is unpreferable because it causes rapid crystal precipitation in the reheating treatment process, thus developing cracks in the glass, or it makes the glass melt to crystallize at the time of being poured into the molds. In contrast, adding a very small amount of MgO makes it difficult for the glass to crystallize in the reheating treatment process.

Al_2O_3 has the effect of improving the water

durability of glass so as to facilitate glass formation, and is also a component of crystals to be formed. It is unpreferable to add a very large amount of Al_2O_3 because it increases the glass melting temperature. It is also unpreferable to add a very large amount of Al_2O_3 because it causes the glass to crystallize rapidly in the reheating treatment process, thus inducing local strain in the glass, and eventually cracks.

The following is a method for evaluating partially crystallized glass thus manufactured. The obtained partially crystallized glass is processed into a substrate of 15 mm×15 mm×1 mm, and the surface is mirror polished so as to measure the transmittance of incident light with wavelengths of 1300 nm to 1600 nm. Then, on the substrate of the partially crystallized glass, SiO_2 films as low refractive index layers and Ta_2O_5 films as high refractive index layers are formed alternately to make a multilayer film filter with a total thickness of 26 μm and a multilayer film filter with a total thickness of 52 μm. These multilayer film filters are cut into a size of 1.5 mm×1.5 mm. The filtering properties of these pieces are evaluated at 20°C and 80°C in wavelengths of 1510 nm to 1580 nm so as to calculate temperature dependence of the amount of wavelength shift.

In addition, the presence or absence of cracks after

the reheating treatment is checked macroscopicly. The thermal expansion coefficient of each glass sample is measured with a thermal mechanical analyzer (TMA). The presence or absence of crystals in the glass is also measured by checking the presence or absence of diffraction peaks in X-ray diffraction measurement. In order to examine the water durability of the glass, first of all, the glass samples are formed into blocks of 10 mm×10 mm×2 mm, and then the surfaces are mirror-polished. These blocks are put in a high-temperature high-humidity chamber of 95°C and 65% of RH to check whether the block surfaces become opaque due to the elution of a glass component.

The compositions, evaluation results and the like of the obtained samples are shown in Tables 1 and 2.

TABLE 1

No.	composition (mol%)						appearance after casting molds	α before reheating ($10^{-7}K^{-1}$)	retention temperature (℃)
	SiO_2	B_2O_3	Na_2O	K_2O	MgO	Al_2O_3			
1	33.0	0.0	15.0	15.0	32.0	5.0	not melt	-	-
2	36.0	3.0	13.0	13.0	30.0	5.0	crystallized	-	-
3	37.5	5.0	12.5	12.5	30.0	5.0	transparent	117.7	540
4	37.5	5.0	11.0	11.0	35.0	5.0	transparent	100.3	530
5	40.0	2.5	12.5	12.5	22.5	10.0	transparent	107.2	570
6	43.0	2.0	12.5	12.5	22.0	8.0	transparent	111.5	550
7	44.0	2.0	12.5	12.5	22.0	7.0	transparent	109.2	590
8	40.0	0.0	15.0	15.0	20.0	5.0	not melt	-	-
9	40.0	1.0	15.0	15.0	19.0	5.0	not melt	-	-
10	40.0	5.0	12.5	12.5	25.0	5.0	transparent	112.3	550
11	40.0	6.0	12.5	12.5	24.0	5.0	transparent	110.1	550
12	42.5	2.5	3.0	22.0	22.0	8.0	not melt	-	-
13	42.5	2.5	6.0	21.0	21.0	7.0	transparent	104.5	600
14	42.5	2.5	6.0	19.0	22.0	8.0	transparent	107.2	630
15	42.5	2.5	8.0	17.0	22.0	8.0	transparent	109.8	600
16	42.5	2.5	10.0	15.0	22.0	8.0	transparent	111.6	570
17	42.5	2.5	15.0	10.0	22.0	8.0	transparent	114.9	560
18	42.5	2.5	17.0	8.0	22.0	8.0	transparent	115.1	580
19	42.5	2.5	19.0	6.0	22.0	8.0	transparent	112.9	570
20	42.5	2.5	20.0	5.0	22.0	8.0	transparent	109.8	560
21	42.5	2.5	21.0	4.0	22.0	8.0	transparent	107.8	560
22	42.5	2.5	23.0	2.0	22.0	8.0	transparent	107.8	560
23	40.0	10.0	7.5	7.5	30.0	5.0	not melt	-	-
24	42.5	2.5	6.0	14.0	30.0	5.0	transparent	99.8	550
25	42.5	2.5	7.0	15.0	28.0	5.0	transparent	101.2	550
26	42.5	2.5	13.0	14.0	23.0	5.0	transparent	121.8	580
27	42.5	2.5	14.0	14.0	22.0	5.0	transparent	129.8	580
28	42.5	2.5	14.0	15.0	21.0	5.0	transparent	137.6	590
29	42.5	2.5	12.5	12.5	20.0	10.0	transparent	112.0	590
30	42.5	2.5	12.5	12.5	21.0	9.0	transparent	111.7	590
31	42.5	2.5	12.5	12.5	25.0	5.0	transparent	111.2	560
32	37.5	2.5	12.5	12.5	30.0	5.0	transparent	111.9	540
33	37.5	2.5	12.5	12.5	31.0	4.0	transparent	111.1	520
34	37.5	2.5	10.0	10.0	38.0	2.0	transparent	110.8	520
35	37.5	2.5	8.5	8.5	41.0	2.0	not melt	-	-
36	42.5	2.5	12.5	12.5	27.5	2.5	transparent	106.9	570
37	42.5	2.5	12.5	12.5	27.0	3.0	transparent	106.5	570
38	40.0	5.0	12.5	12.5	25.0	5.0	transparent	115.8	620
39	41.0	2.5	12.5	12.5	21.5	10.0	transparent	107.2	630
40	40.0	2.5	12.5	12.5	21.5	11.0	transparent	106.8	630
41	40.0	2.5	10.0	12.5	22.0	13.0	not melt	-	-

TABLE 2

No.	appearance after reheating	crystal precipitation	Weather-ing	α after re-heating ($10^{-7}K^{-1}$)	internal trans-mittance (%)	wave-length shift 1 (pm/℃)	wave-length shift 2 (pm/℃)
3	faintly opaque	A, B	none	142.0	97.1	-2.0	-0.1
4	faintly opaque	A, B	none	126.0	97.5	-0.1	1.9
5	faintly opaque	A, B	none	129.0	97.9	-0.2	1.7
6	faintly opaque	A, B	none	135.7	98.6	-1.7	0.2
7	transparent	none	none	109.4	99.4	2.1	4.0
10	faintly opaque	A, B	none	126.0	97.7	-0.2	1.6
11	transparent	none	none	109.8	97.9	1.6	3.8
13	faintly opaque	A, B	present	165.0	98.0	-3.2	-1.2
14	faintly opaque	A, B	none	151.0	97.5	-2.5	-0.6
15	faintly opaque	A, B	none	147.1	97.1	-2.6	-0.6
16	faintly opaque	A, B	none	147.2	97.8	-2.5	-0.7
17	faintly opaque	A, B	none	138.1	97.3	-1.7	0.2
18	faintly opaque	A, B	none	131.2	97.2	-0.9	0.9
19	faintly opaque	A, B	none	123.8	97.2	0.2	2.0
20	faintly opaque	A, B	none	120.5	97.2	0.3	2.3
21	faintly opaque	A, B	none	118.2	97.1	0.6	2.5
22	transparent	A, B	present	120.0	-	-	-
24	faintly opaque	A, B	none	122.5	97.7	0.4	2.2
25	faintly opaque	A, B	none	127.8	97.7	-0.4	1.6
26	faintly opaque	A, B	none	143.2	97.6	-2.3	-0.3
27	faintly opaque	A, B	present	147.8	97.6	-2.5	-0.5
28	faintly opaque	A, B	present	153.4	97.7	-2.8	-0.9
29	transparent	none	none	112.8	99.8	1.5	3.5
30	faintly opaque	A, B	none	138.8	98.3	-1.8	0.4
31	faintly opaque	A, B	none	140.4	98.4	-2.0	-0.1
32	faintly opaque	A, B	none	142.3	97.5	-2.2	-0.2
33	faintly opaque	A, B	none	144.1	97.5	-2.3	-0.2
34	cracks	A, B	none	-	-	-	-
36	transparent	none	none	107.7	98.5	2.3	4.0
37	faintly opaque	A, B	none	139.2	98.3	-1.7	0.4
38	faintly opaque	A, B	none	130.8	97.9	-0.6	0.9
39	faintly opaque	A, B	none	135.4	97.9	-1.5	0.5
40	cracks	A, B	-	-	-	-	-

In the column of crystal precipitation in Table 2, "A" represents $K_{1.25}Al_{1.25}Si_{0.75}O_4$, and "B" represents $KAlSiO_4$.

As in Sample 2, when the SiO_4 content is less than 37 mol%, the glass melt crystallizes at the time of being

poured into the mold. In contrast, as in Sample 7, when the content exceeds 43 mol%, the glass does not crystallize in the reheating treatment process.

As in Samples 8 and 9, when the B_2O_3 content is less than 2 mol%, the melting temperature is too high to obtain uniform glass. In contrast, as in Sample 11, when the content exceeds 5 mol%, the glass does not crystallize in the reheating treatment process.

As in Sample 12, when the Na_2O content is less than 5 mol%, the mixture of glass ingredients does not melt uniformly. In contrast, as in Samples 21 and 22, when the content exceeds 20 mol%, the linear expansion coefficient does not reach $125\times10^{-7}K^{-1}$ even after the glass is partially crystallized. As in Samples 19 and 20, when the K_2O content is less than 7 mol%, the linear expansion coefficient is not large enough even after the glass is partially crystallized. In contrast, as in Sample 13, when the content exceeds 20 mol%, the water durability of the glass decreases. As in Samples 23 and 24, when the sum of the Na_2O content and the K_2O content is less than 21 mol%, the mixture of glass ingredients does not melt uniformly or the linear expansion coefficient of the partially crystallized glass is not large enough. On the other hand, as in Samples 27 and 28, when the sum of the contents exceeds 27 mol%, the

water durability of the glass decreases.

As in Sample 29, when the MgO content is less than 21 mol%, crystal precipitation does not occur in the glass after the reheating treatment. In contrast, as in Samples 34 and 35, when the content exceeds 37 mol%, crystal precipitation occurs rapidly in the reheating treatment process, thus inducing cracks in the glass. When the MgO content is particularly large, the glass melt crystallizes at the time of being poured into the molds.

As in Sample 36, when the Al_2O_3 content is less than 3 mol%, crystal precipitation does not occur in the glass in the reheating treatment process. In contrast, as in Sample 40, when the content exceeds 10 mol%, crystal precipitation occurs rapidly in the reheating treatment process, thus inducing cracks in the glass. When the content is particularly large, it is difficult to melt the mixture of glass ingredients as in Sample 41.

In the samples having crystal precipitation, the precipitated crystals are mainly potassium aluminum silicate base $K_{1.25}Al_{1.25}Si_{0.75}O_4$ or $KAlSiO_4$. The precipitation of these crystals increases the linear expansion coefficient, as compared with the glass that has not been crystallized yet.

The following is a description about the influence

of the retention time in the reheating treatment process and the rate of the slow cooling subsequent to the reheating treatment process on the thermal expansion coefficient and transmittance of the partially crystallized glass. As an example, of the samples shown in Table 1, the glasses of Samples 5, 6, 13-19 and 38 are used to measure the thermal expansion coefficient and transmittance value of the partially crystallized glasses which are obtained while changing the retention time and slow cooling rate. The results are shown in Tables 3 and 4.

TABLE 3

No.	retention temperature (℃)	retention time (h)	cooling rate (℃/h)	appearance	α after reheating ($10^{-7}K^{-1}$)	trans-mittance (%/mm)
5	550	1	-10	transparent	106.0	99.3
	560	1	-10	cracks	-	-
	570	1	-10	faintly opaque	129.0	97.9
	580	1	-10	faintly opaque	126.0	97.1
	590	1	-10	cracks	-	-
	600	1	-10	faintly opaque	121.0	96.0
	540	10	-10	cracks	-	-
	550	1	-10	cracks	-	-
6	510	10	-10	transparent	110.9	99.4
	520	10	-10	faintly opaque	116.2	98.9
	530	10	-10	faintly opaque	134.5	98.8
	550	10	-10	faintly opaque	135.7	98.6
13	540	5	-100	transparent	115.7	99.5
	560	5	-100	faintly opaque	145.5	97.9
	580	5	-100	cracks	-	-
	600	5	-100	faintly opaque	165.0	98.0
	620	5	-100	faintly opaque	159.7	
	590	0.5	-10	cracks	-	-
	600	0.5	-10	cracks	-	-
	620	0.5	-10	faintly opaque	162.9	98.1
14	590	5	-100	transparent	106.3	99.1
	620	5	-100	faintly opaque	148.0	97.8
	630	5	-100	faintly opaque	151.0	97.5
	640	5	-100	faintly opaque	144.9	97.0
	570	2	-5	faintly opaque	162.9	97.7
	575	2	-5	faintly opaque	162.0	97.5
15	540	5	-100	transparent	113.7	99.1
	580	5	-100	faintly opaque	148.7	97.2
	600	5	-100	opaque	143.7	84.2
	560	5	-100	cracks	-	-
	590	1	-10	faintly opaque	141.7	97.5
	600	1	-10	faintly opaque	147.1	97.1
	580	2	-5	faintly opaque	151.0	97.1

TABLE 4

No.	retention temperature (℃)	retention time (h)	cooling rate (℃/h)	appearance	α after reheating ($10^{-7}K^{-1}$)	trans-mittance (%/mm)
16	540	5	-100	transparent	113.7	99.3
	570	5	-100	faintly opaque	147.2	97.8
	580	5	-100	faintly opaque	143.6	97.1
	590	5	-100	faintly opaque	143.7	96.4
	560	5	-100	cracks	-	-
17	530	5	-100	faintly opaque	129.3	98.2
	540	5	-100	faintly opaque	133.1	97.6
	560	5	-100	faintly opaque	138.1	97.3
	570	5	-100	faintly opaque	133.0	96.8
	580	5	-100	faintly opaque	133.5	95.1
18	540	5	-100	faintly opaque	127.6	97.8
	580	5	-100	faintly opaque	134.2	97.2
	590	5	-100	faintly opaque	124.9	96.1
19	530	5	-100	faintly opaque	127.8	97.8
	540	5	-100	faintly opaque	129.4	97.6
	560	5	-100	faintly opaque	129.1	97.5
	570	5	-100	faintly opaque	133.8	97.2
	580	5	-100	faintly opaque	129.1	95.4
38	520	5	-100	transparent	113.4	99.4
	550	5	-100	transparent	103.5	99.4
	600	5	-100	transparent	113.3	99.0
	610	5	-100	faintly opaque	120.7	98.2
	620	5	-100	faintly opaque	130.8	97.9

As shown in Tables 3 and 4, as a whole, when the retention temperature in the reheating treatment process is very low, there is no crystal precipitation, whereas when the temperature is very high, too much crystal is precipitated, thus greatly decreasing the transmittance. In Samples 6 and 38, the thermal expansion coefficient increases with decreasing transmittance, but it hardly changes from a certain point forward. In Samples 5 and 13-19, the thermal expansion coefficient begins to decrease from a certain point forward.

By thus optimizing the retention temperature and slow cooling rate in the reheating treatment process, partially crystallized glass can be obtained in a stable manner without causing local strain or cracks. In addition, a maximum thermal expansion coefficient and sufficiently high transmittance of the partially crystallized glass can be maintained. This results in partially crystallized glass effective to reduce the temperature dependence of the wavelength shift which is usually positive in a multilayer film filter.

INDUSTRIAL APPLICABILITY

As described hereinbefore, the present invention provides partially crystallized glass which is made up of SiO_2, B_2O_3, Na_2O, K_2O, MgO and Al_2O_3, and which has a mean thermal expansion coefficient not lower than $125\times10^{-7}K^{-1}$ in the temperature range of 50°C to 150°C. In this partially crystallized glass, potassium aluminum silicate base crystals are precipitated in some parts of the glass, so that the thermal expansion coefficient is high. Therefore, using the glass as a substrate for a multilayer film filter can fully reduce temperature fluctuations in the filter properties.